Photo-induced Charge Transfer in Azapyrene-Tetrathiafulvalene Triads

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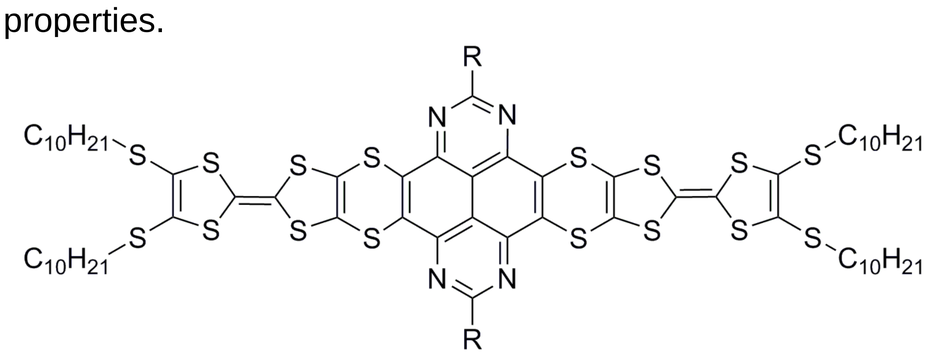
Abstract: Tetraazapyrene (TAP) and its *tert*-butyl substituted derivative are symmetrically functionalised with two tetrathiafulvalene (TTF) units. Electronic communication between TTF units and the central TAP core in resultant triads is evaluated by UV-Vis absorption, cyclic voltammetry and spectroelectrochemical measurements. Notably, the insertion of *tert*-butyl groups raises the TAP-localised LUMO level by 0.21 eV.

Introduction: Tetraazapyrene (TAP), the prototype of nitrogenated polycyclic aromatic hydrocarbons (N-PAHs), exhibits intrinsic optoelectronic and electrochemical properties as well as high thermal and chemical stability, all important requirements for its diverse applications in the field of organic (opto)electronics.[1,2] However, only quite limited reports on synthetic approaches to the TAP scaffold and its derivatization appear in the literature. In 2012, a series of 2,7-substituted TAP derivatives was prepared and tested as n-type semiconductors in organic field-effect transistors (OFETs).[1] It has been demonstrated that the electronic properties are significantly affected by the nature of substituents at the core positions. Inspired by these appealing results, we have embarked on the design and synthesis of tetrathiafulvalene (TTF)-functionalized TAPs to create novel triads (Scheme 1) with promising material properties.



TTF-TAP R=H**; TTF-*t*-Bu-TAP** R=*tert*-butyl

Scheme 1 Chemical structures of the **TTF-TAP** and **TTF-*t*-Bu-TAP**.

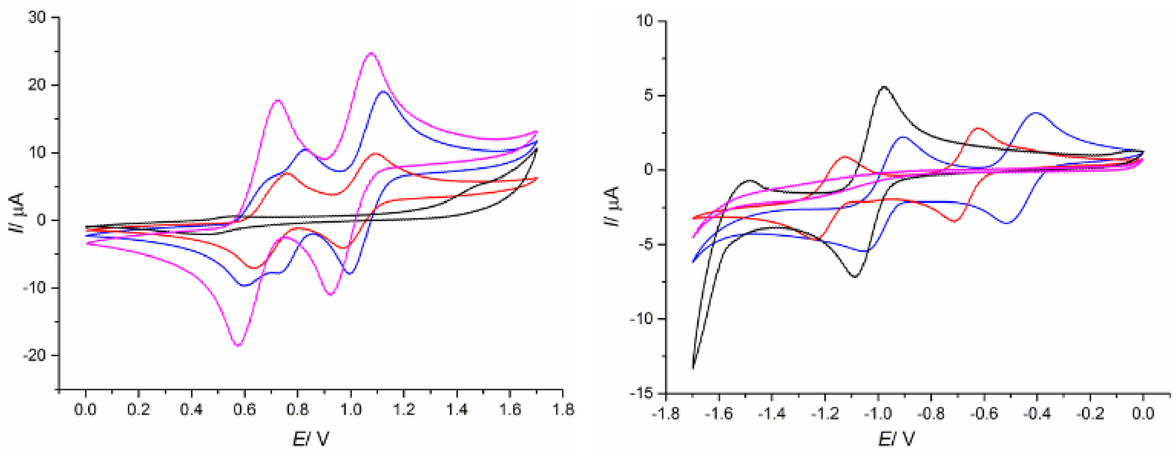


Figure 1. Differential Cyclic voltammograms of **TTF-TAP** (blue), **TTF-*t*-Bu-TAP** (red), *t*-Bu-TAP (black) and TTF precursor (pink) were measured in dichloromethane solution, containing 0.1 M $TBAPF_6$ as the supporting electrolyte at room temperature, Pt working electrode, Ag/AgCl electrode as the reference electrode and the scan rate at 100 mV s^{-1}.

Figure 1 shows that **TTF-TAP** undergoes three distinct reversible oxidation processes at 0.63 V, 0.77 V and at 1.06 V (*vs* Ag/AgCl), indicating that two TTF units are successively oxidized to TTF radical cation species and simultaneously to TTF dication species. This splitting into two oxidation processes for the generation of its radical cation points to intramolecular through-bond interactions between two TTF units. In the negative potential window, two reversible reduction waves at -0.46 V and -0.98 V are observed, corresponding to sequential addition of electrons to the TAP unit. Interestingly, the incorporation of *tert*-butyl group has an appreciable influence on the redox properties of TTF and TAP units. **TTF-*t*-Bu-TAP** shows only two reversible oxidation waves at 0.70 V and 1.03 V, suggesting that two TTF units are simultaneously oxidized to their radical cation and dication species, respectively. It also undergoes two reversible reductions at -0.67 V and -1.19 V, which, however, are negatively shifted compared to TTF-TAP. Consequently, the insertion of *tert*-butyl groups raises the LUMO level by 0.21 eV, very probably due to the hyperconjugation and electron-donating effect of the tert-butyl groups.

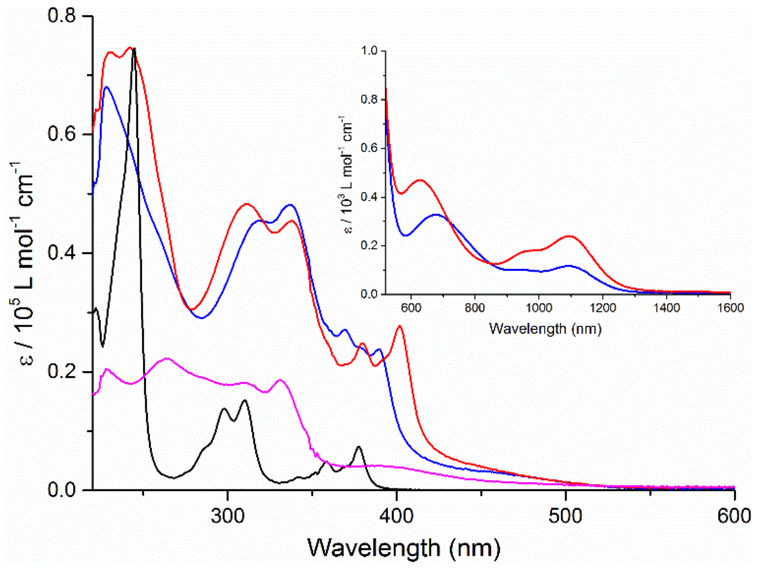


Figure 2. UV-Vis absorption spectra of **TTF-TAP** (blue), **TTF-*t*-Bu-TAP** (red), *t*-Bu-TAP (black) and TTF precursor (pink) in CH_2Cl_2 at r.t. Insert: Vis-NIR absorption spectra of **TTF-TAP**, **TTF-*t*-Bu-TAP** in CH_2Cl_2 at r.t.

In the UV and blue part of the optical spectra, the observed strong absorption bands are attributed to π–π* transitions localized on the TTF and TAP cores, only with bathochromic shifts owing to some extended conjugation. By comparison of **TTF-*t*-Bu-TAP** (red) to **TTF-TAP** (blue), the insertion of the *tert*-butyl groups leads to noticeable bathochromic shifts of the absorption bands in a range of 360 nm and 450 nm and a slight hypsochromic shift of the absorption band around 320 nm. As these transitions correspond mainly to π–π* excitations of the TAP core, the observed shifts can be accounted for by the fact that the presence of bulky *tert*-butyl groups at 2,7-positions of the TAP is unfavorable for possible *H*- and *J*-aggregation and impedes effective intermolecular interactions. More importantly, both triads exhibit two weak and broad absorption bands centered at 680 nm and 1100 nm for **TTF-TAP**, and 630 nm and 1100 nm for **TTF-*t*-Bu-TAP**. Consequently, these absorptions reflect ICT transitions dominated by excitations from HOMOs localized on the TTF units to the LUMO localized on the TAP core.

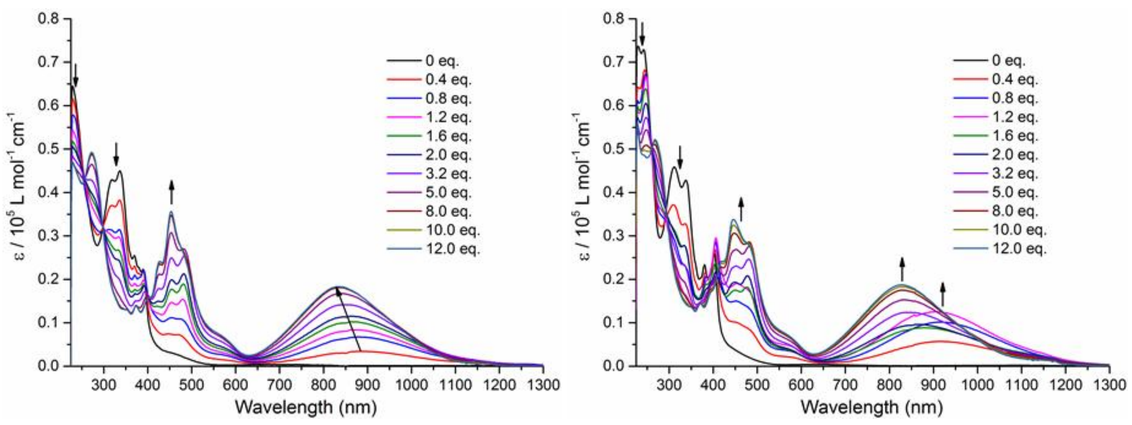


Figure 3. Variation of UV-Vis-NIR absorption spectra of **TTF-TAP** (left) and **TTF-*t*-Bu-TAP** (right) in CH_2Cl_2 upon successive addition of aliquots of $NOSbF_6$ at room temperature.

As shown in Fig. 3 for **TTF-TAP**, a progressive reduction of the absorbance of high energy of π–π* transitions is accompanied with a concomitant appearance of new absorption bands peaked at 452 nm and 835 nm which reach their maximum values upon addition of 12 equiv. of $NOSbF_6$. The lowest energy absorption band is continuously blue-shifted during the oxidation process. These new transitions are characteristic of the newly formed cationic TTF radical $TTF^{\cdot+}$ within a D-A-D triad. In contrast, the initial oxidation of **TTF-*t*-Bu-TAP** leads to a broad absorption band which emerges at 905 nm, and after addition of 1.2 equiv. suddenly moves towards higher energy (830 nm) with increasing amounts of $NOSbF_6$.

Conclusion: Both **TTF-TAP** and **TTF-*t*-Bu-TAP** absorb in the UV-Vis-NIR spectral region due to ICT excitations from TTF units to the central TAP core. Upon chemical oxidation, a reverse ICT from the TAP core to the $TTF^{\cdot+}$ moieties occurs. Interestingly, the two TTF units of **TTF-TAP** and **TTF-*t*-Bu-TAP** are sequentially and simultaneously oxidized to the TTF radical cation species, respectively.

REFERENCES

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